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Diagnostic Testing and Analysis Toward Understanding Aging Mechanisms and Related Path Dependence

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Overview

Timeline	Barriers
Project Start: April 2008 **Project End:** Ongoing **Percent Complete:** ≈ 90%. (Based on remaining funding between INL and U. Hawaii)	**Cell/battery Life and related path dependence** **— lack of accurate life prediction capabilities** **Abuse Tolerance, Reliability and Ruggedness**
Budget	**Partners**
Funding Received: **FY 12: $ 700K** **(includes subcontracts)** **FY13: $ 300K**	**Hawaii Natural Energy Institute (HNEI) at University of Hawaii at Manoa** **Argonne National Lab**

Relevance

Long-term usage of lithium-ion batteries in vehicle applications represents a significant warranty commitment and a long-term safety risk. Yet, there is insufficient knowledge regarding prolonged aging processes in such batteries, particularly in cases of strong path dependence of aging.

Our objectives include:

- Establish a platform of Developmental & Applied Diagnostic Testing (DADT) designed for particular issues in EDV batteries:
  - defined by application-specific performance.
- Employ DADT to examine mechanistic contributions to cell aging.
- Utilize DADT results to support advanced prognostic life modeling tools.
- Utilize DADT knowledge to support improvement of materials.
- Apply DADT to series strings of cells to understand string aging dynamics.
- Develop/optimize an operational protocol to minimize the aging process (chemistry-specific, but with generalized approach).

Our overarching goal is to understand the mechanistic progression of aging for batteries in their *intended applications*, and provide a foundation for improving cell materials and minimizing aging rates.

Milestones

Milestone	Status	Date
INL Path Dependence Studies 1 and 2: • Daily Thermal Cycling superimposed onto PHEV cell cycling • Power Pulse Performance Hysteresis	Completed	Study1: Dec. 2012 Study2: Mar. 2013
Modeling in support of aging mechanisms and path dependence	Completed	March 2013
Pouch Cell Pressure Management to Increase Life: Gen2 Fixture	Completed	March 2013
Pouch Cell Pressure Management to Increase Life: Baseline Tests	Ongoing	
Supplemental DADT (INL): • Current conditioning to prolong cell life • Self-discharging behavior and mechanisms	Follow-on work Completed	Feb. 2013
Multi-cell String Evaluation and Diagnosis (data and simulations) for 3S1P configuration (HNEI),	Completed	March 2012
Diagnostic Emulation Modeling Tool for Degradation Modes Simulation (mechanistic inference technique) (HNEI)	Follow-on work Completed	July 2012
Additional string-level studies per degradation tied to cell-to-cell interactions and variations (HNEI and INL)	Phase 2 Ongoing	

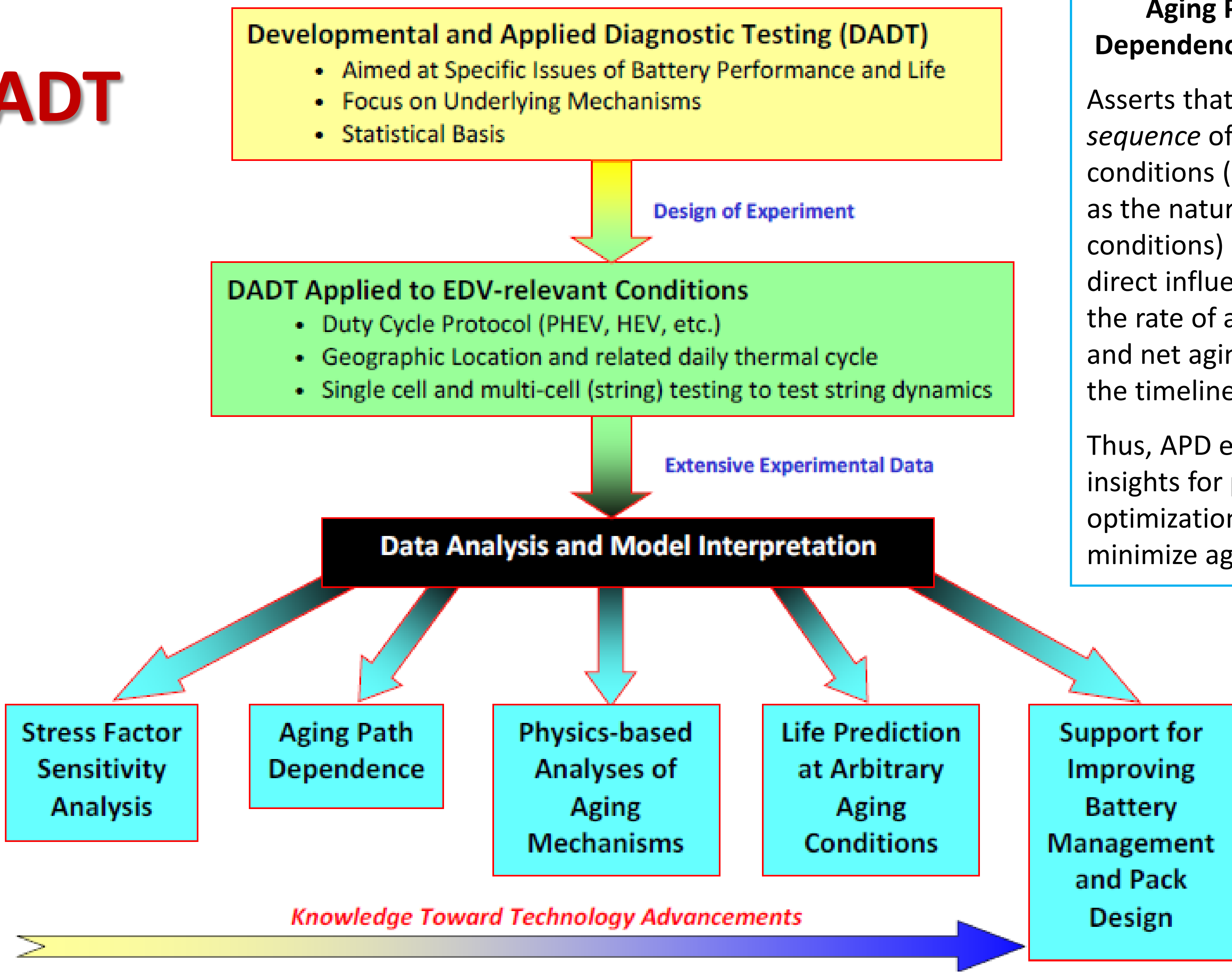
Approach

Developmental & Applied Diagnostic Testing (DADT)
Why DADT?

- We seek to understand how cells, strings, and packs ***age in their intended applications.*** For EDVs this would entail aging factors for lithium-ion cells such as nature and frequency of duty cycles, frequency and severity of daily and annual thermal cycles, thermal management parameters, and multi-cell string dynamics.
- DADT permits **identification/isolation of degradation mechanisms** and **conditions of reduced performance** to yield unique technology thumbprints. From this we can optimize battery use to mitigate severe limitations and prolong battery life.
- **Aging path dependence** can be evaluated, aiding in **more sophisticated battery use roadmaps**, and **better prognostics**.
- DADT is **essential toward physics-based models** of aging and performance.
- Through DADT, **technology vetting is deepened, TRLs are better assessed, and technology deployment is accelerated**.

Approach

DADT



Key DADT Target:

Aging Path Dependence (APD)

Asserts that the *sequence* of aging conditions (as well as the nature of conditions) has a direct influence on the rate of aging and net aging along the timeline.

Thus, APD enables insights for path optimization to minimize aging.

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Li-ion Chemistry Used for Many Studies: Sanyo 'Y'

Configuration: 18650
Cathode: $\{LiMn_2O_4 + LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2\}$
Anode: graphitic
V_{max} = 4.2 V (100% SOC)
V_{min} = 2.7 V (0% SOC)
90% SOC = 4.07 V
70% SOC = 3.94 V
35% SOC = 3.65 V
Electrode Area: 800 cm^2 (estimated)
$C_1/2$ discharge capacity: 1.9 Ah,
$C_1/1$ discharge capacity: 1.86 Ah
Maximum recommended continuous discharge current: 5.7A
Maximum operating temperature during discharge: 60 °C.

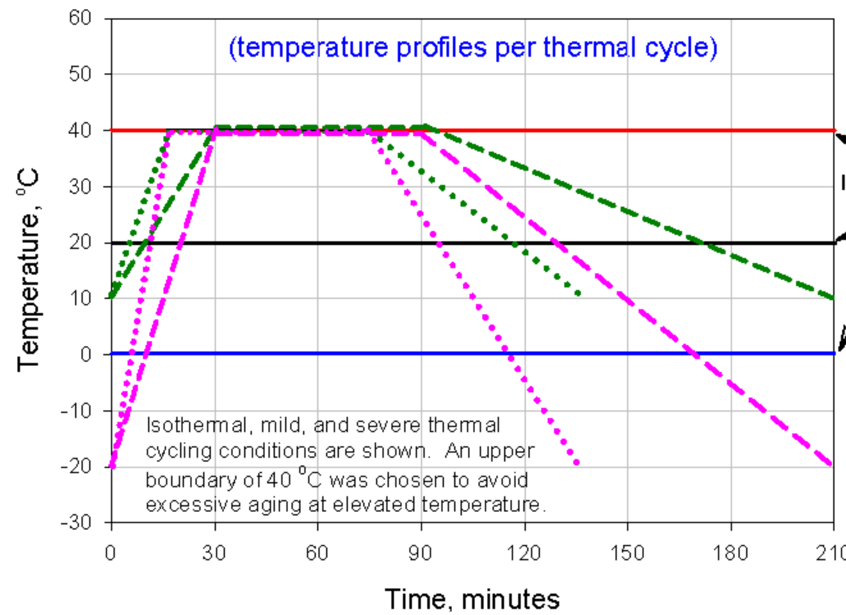
These cells are high quality, economical, and show good stability and low cell-to-cell variability.

Approach

Path Dependence Study 1:

Is there an aging path dependence due to cells operating under both active PHEV cycling and ambient temperature ramping?

The main parameters are (1) the magnitude and frequency of the thermal cycling, looking at *isothermal*, *mild*, and *severe* scenarios, and (2) frequency of duty cycle.

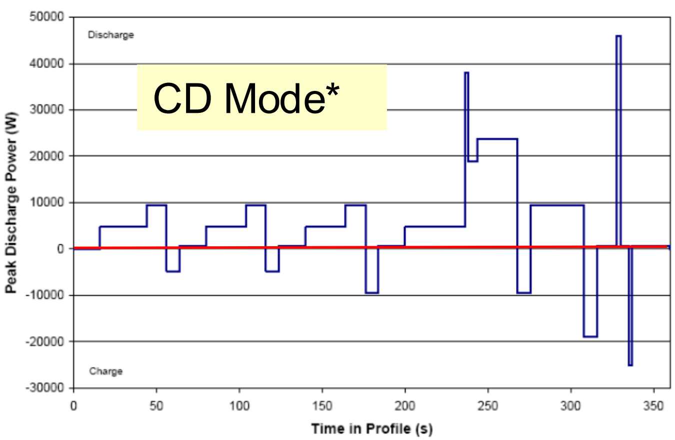


Duty Cycle where

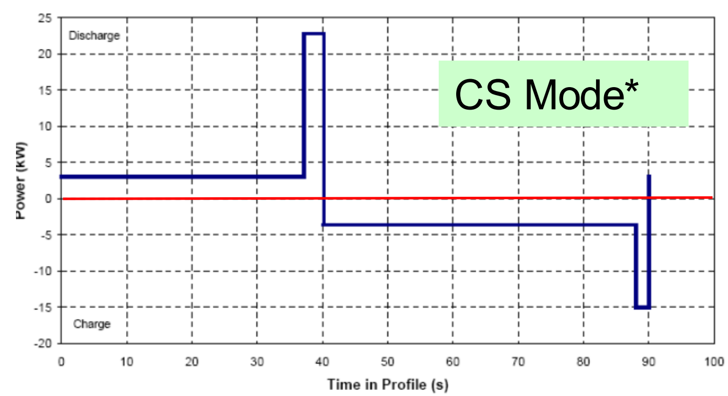
- CD_1 (SOC_0 to SOC_1), then ten CS at SOC_1
- \+ CD_2 (SOC_1 to SOC_2), then ten CS at SOC_2
- \+ CD_3 (SOC_2 to SOC_3), then ten CS at SOC_3,*

Cycle-life Profiles

$SOC_0 > SOC_1 > SOC_2 > SOC_3$ ($\geq SOC_{min}$, here 35%)



Charge-Depleting Cycle Life Test Profile for Maximum PHEV Battery

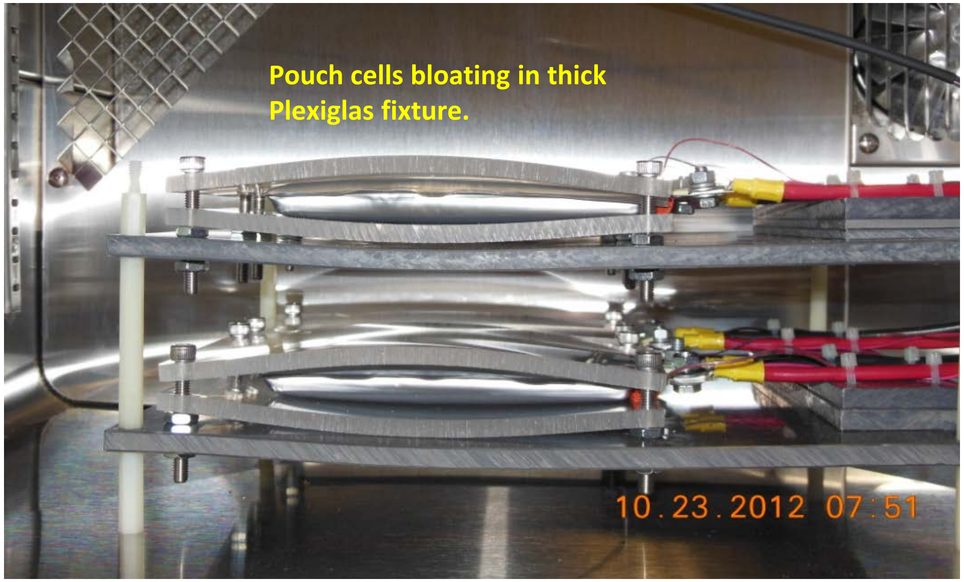


Charge-Sustaining Cycle Life Test Profile (50 Wh) for Maximum PHEV Battery

- This is a valuable study in transitioning between idealized lab data and actual PHEV field data.
- Temperature and cycling parameters can be tailored for specific regional targets.
- Added value is gotten through INL/HNEI synergy.

* Battery Test Manual for Plug-in Hybrid Electric Vehicles (INL, March 2008, rev0).

Pouch Cell Pressure Management to Increase Life: Gen2 Fixture



- Pouch cell pressure management is a critical need!
- A bloated pouch cell produces *worthless data* and is *unsafe*. It is an all-around waste of resources to test or deploy pouch cells without proper pressure management.

The lack of applied pressure can be a unpredictable stress factor for pouch cell aging.

- **INL has initiated DADT protocol that will help standardize and optimize pressure management. This has received strong interest from Industry.**
- **A small scoping study is underway to underscore benefits from pressure management.**

Technical Accomplishments & Progress

- DADT studies have been performed at INL and HNEI that involve well over 100 commercial lithium-ion cells, with most testing completed.
- INL and HNEI DADT studies are isolating the effects of foremost operational parameters on the aging path. Through DADT we develop strategic testing to determine many aspects of how cells will age in their intended application (here, PHEV). In 2012 DADT work progressed within the following areas:

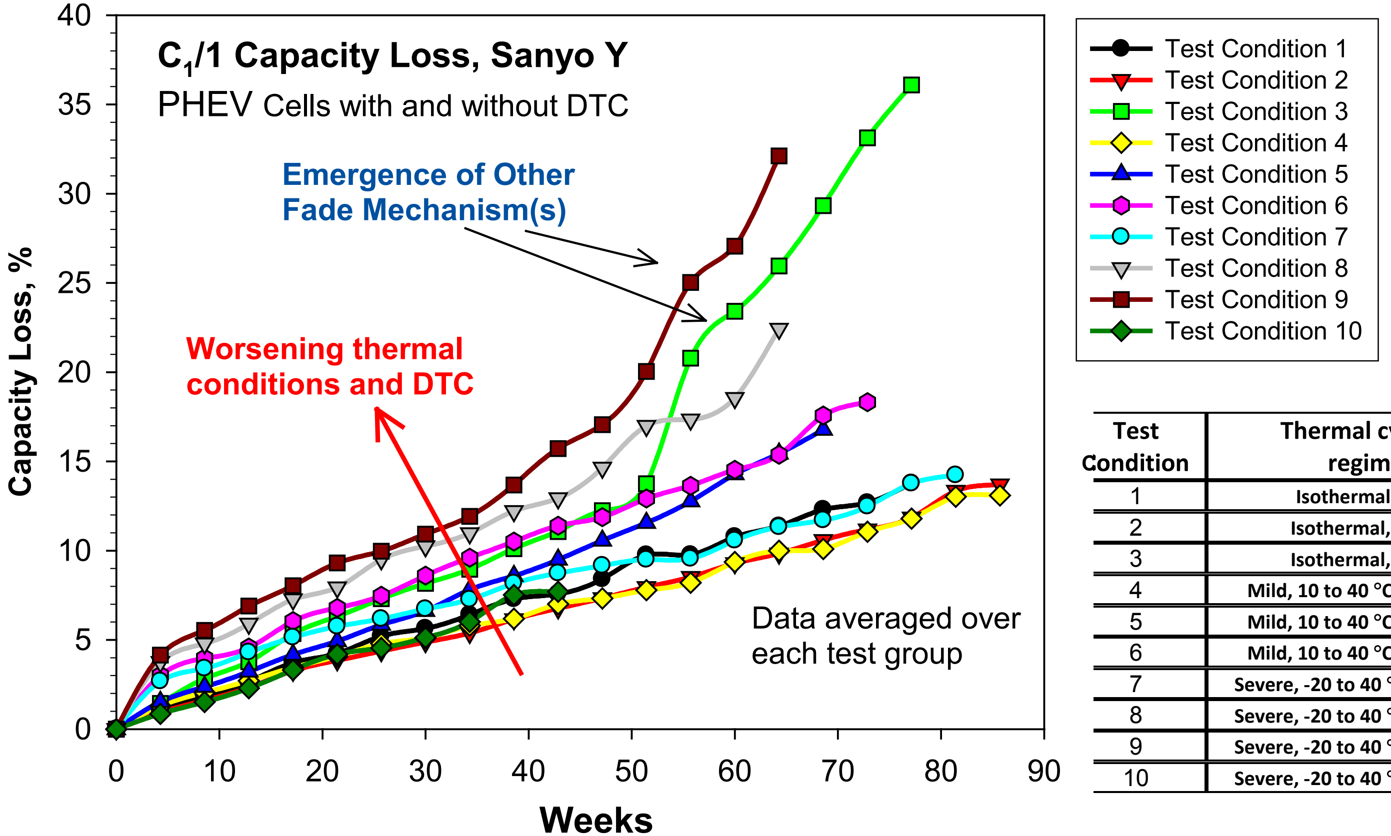
  - Daily Thermal Cycling (DTC) coupled with PHEV cell cycling
  - Power Pulse Performance Hysteresis/Aging
  - Pouch Cell Pressure Management to Increase Cell Life
  - Supplemental & Supporting Studies
    - Current conditioning to prolong cell life
    - Self-discharging mechanisms, quantitative analysis
  - INL CellSage model can be applied to diagnostic and prognostic evaluation of the impact of cell anomalies within strings.

  - Multi-cell String Evaluation and Diagnosis (data and simulations), HNEI
  - Degradation Modes Simulation (mechanistic inference technique), HNEI.
  - Mechanistic Diagnostics with Quantifiable Results and Symptom Presentations, HNEI.

****Numerous papers were either published, submitted or drafted in this period.***

Path Dependence Study 1

These results suggest that EDV batteries operated at colder climates will undergo additional degradation possibly due to particle fracturing from excessive stress, and should have more sophisticated thermal management.



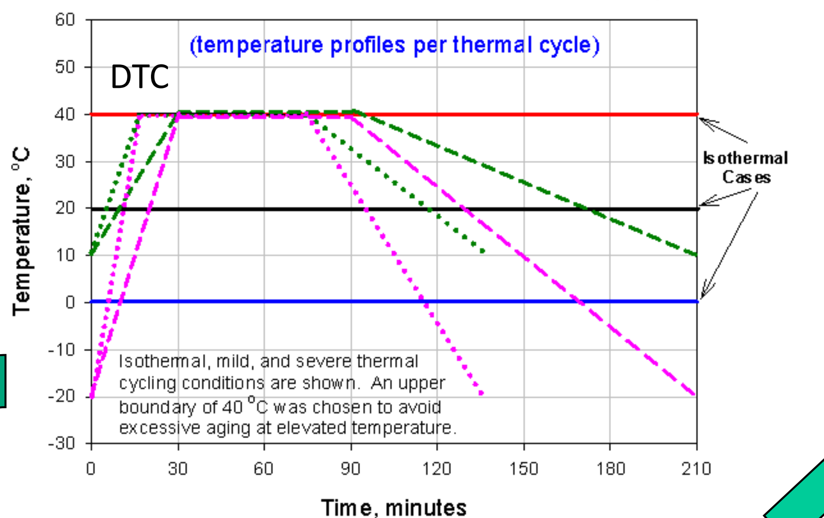
Test Condition	Thermal cycling regime	Duty cycle frequency
1	Isothermal, 0 °C	Continuous
2	Isothermal, 20 °C	Continuous
3	Isothermal, 40 °C	Continuous
4	Mild, 10 to 40 °C in 30 min.	1 Round trip/day
5	Mild, 10 to 40 °C in 30 min.	Continuous
6	Mild, 10 to 40 °C in 15 min.	Continuous
7	Severe, -20 to 40 °C in 30 min.	1 Round trip/day
8	Severe, -20 to 40 °C in 30 min.	Continuous
9	Severe, -20 to 40 °C in 15 min.	Continuous
10	Severe, -20 to 40 °C in 30 min.	None (cal-L)

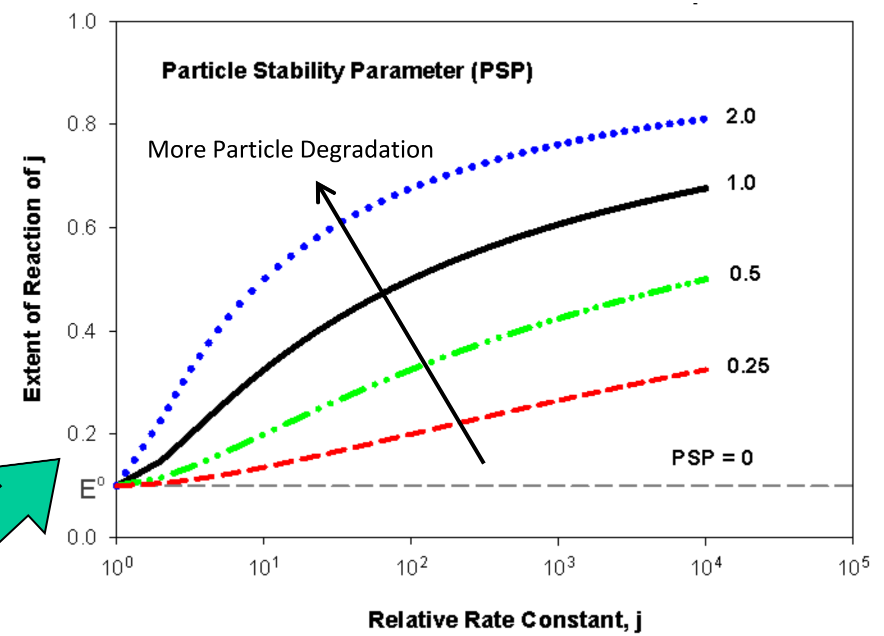
Thermal cycling effects on capacity loss are more evident for cells actively undergoing duty cycles. In contrast, cells under calendar-life conditions and thermal cycling experience slower aging (Condition 10). The results clearly indicate the need to test past one year!

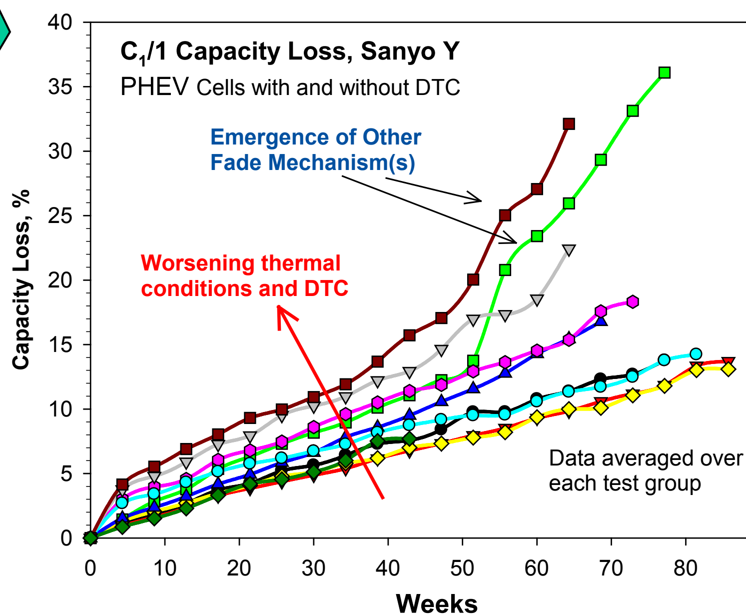
Daily Thermal Cycling (DTC)

From Cold-start to Operating T

Model describes influence of DTC on extent of each j degradation mechanism







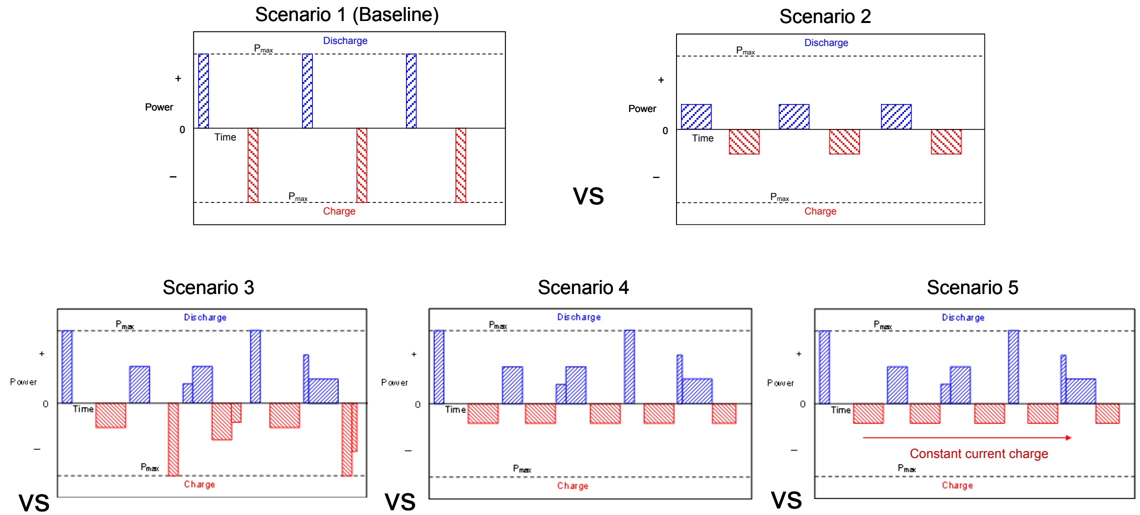
- **PSP represents the relative susceptibility of electrode particles to mechanical degradation (fracturing and breakup) under the conditions of combined electrochemical and thermal cycling.**
- **This factor is related to particle sizes and bulk shape factors, in terms of accessible area per unit volume, given a particle shape, as well as to mechanical stress-strain response of the materials.**

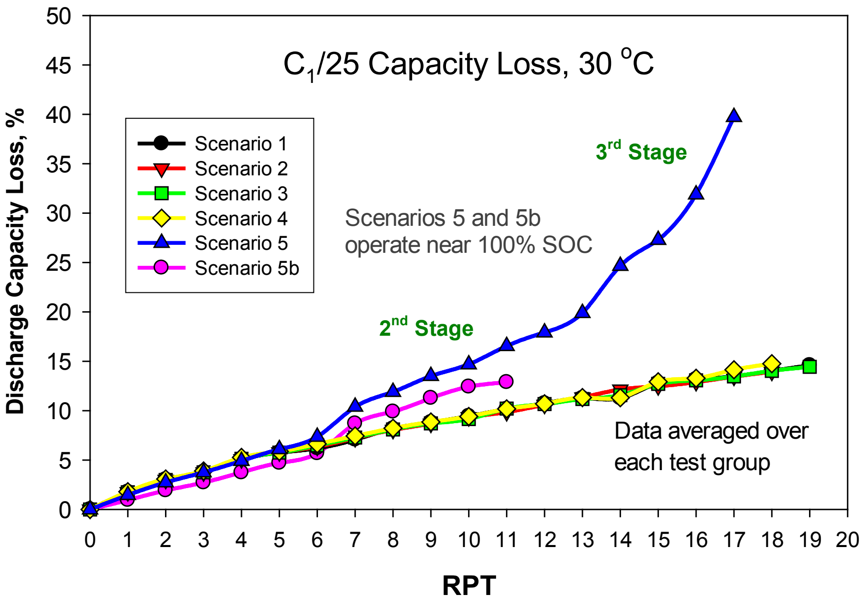
The term E^o is the reaction extent without influence from DTC, arbitrarily given a value of 0.1 here for demonstration purposes. A value of unity is assumed for $a_{j,BL}$ for demonstration purposes.

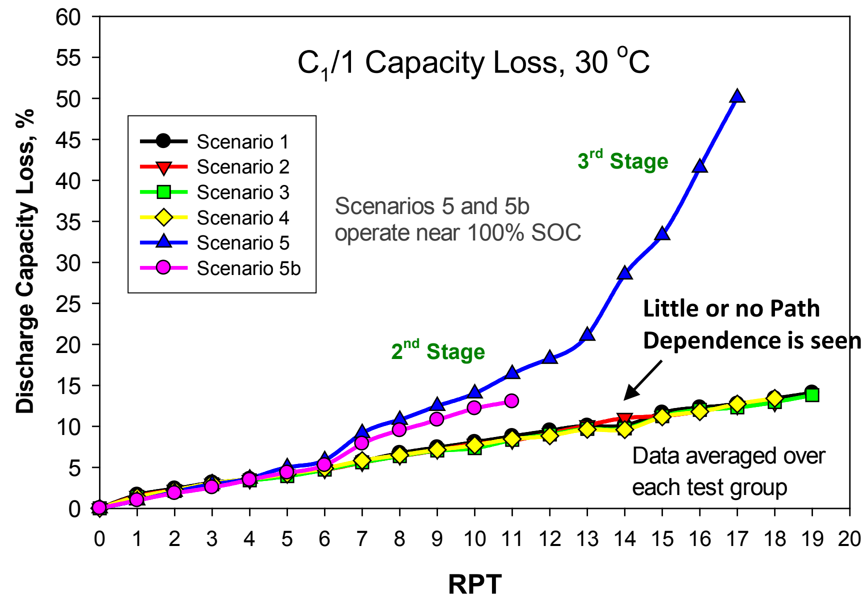
Tech. Accomp. & Progress

Path Dependence Study 2:

Is there aging path dependence due to severity and randomness of power pulses?

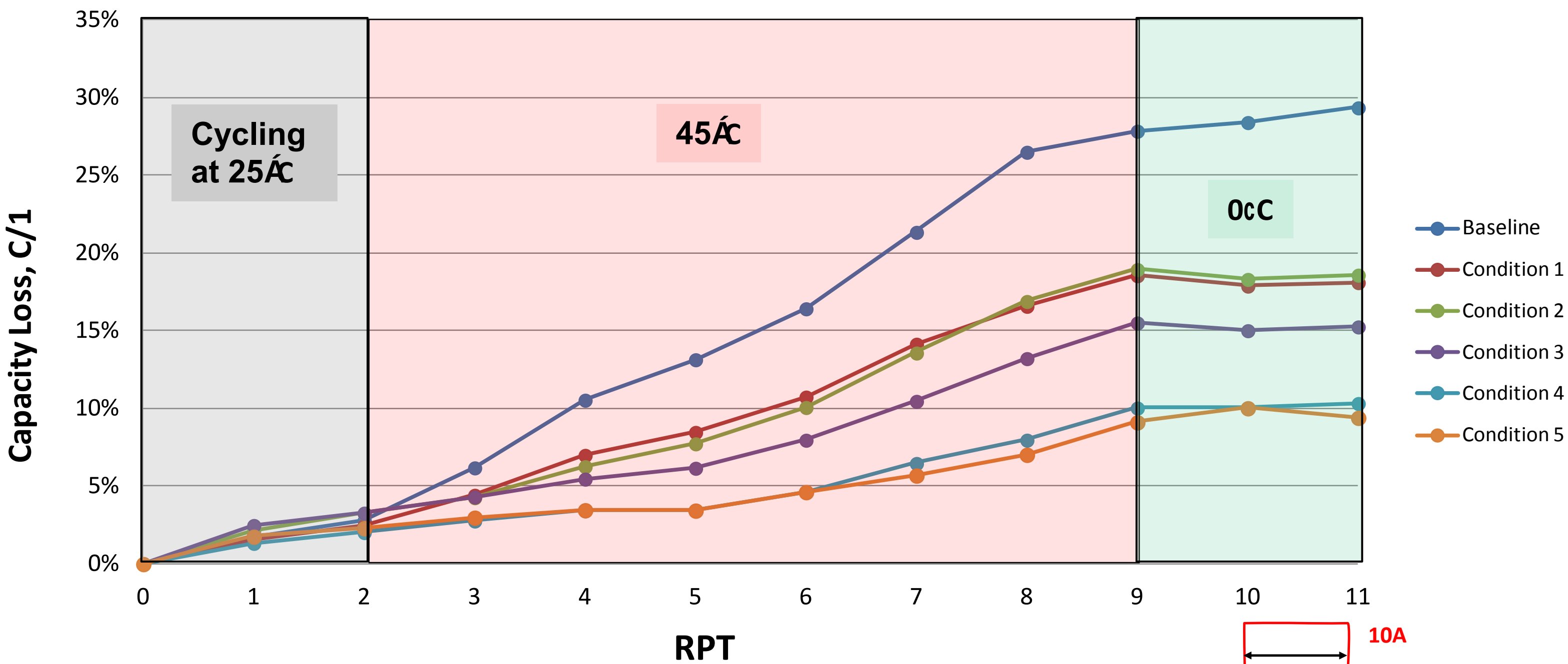




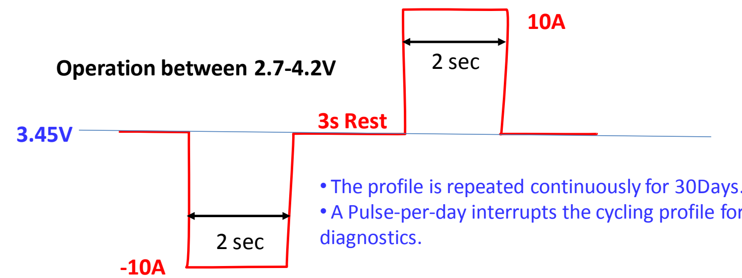


The data shows how these cells are charge sensitive when operated near 100% SOC (Scenarios 5 and 5b). Testing past 12 months is crucial for detecting later stages of degradation!

Prolonging Cell Life through Current Conditioning

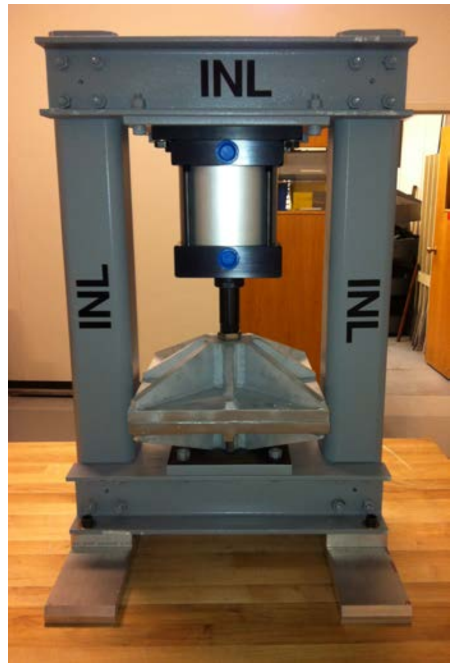


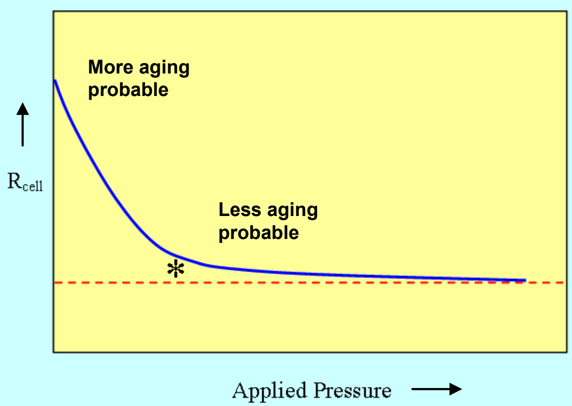
Basic power-pulse "duty cycle" is identical for all test conditions:



INL test results indicate that current conditioning can profoundly diminish the extent of aging up to ⅓ that of baseline cells (Sanyo Y). INL Patent Pending.

Gen2 Pouch Cell Pressurized Fixture





Shown here is the general principle of adding pressure to pouch cells to reduce cell impedance and to standardize the pressure at which cells should be tested and utilized. The inflection point (*) is the point at which adding more pressure does not produce further significant decrease in impedance. Having pressure close to (*) will help inhibit gas formation while pressure far past the inflection may cause physical damage to the cell.

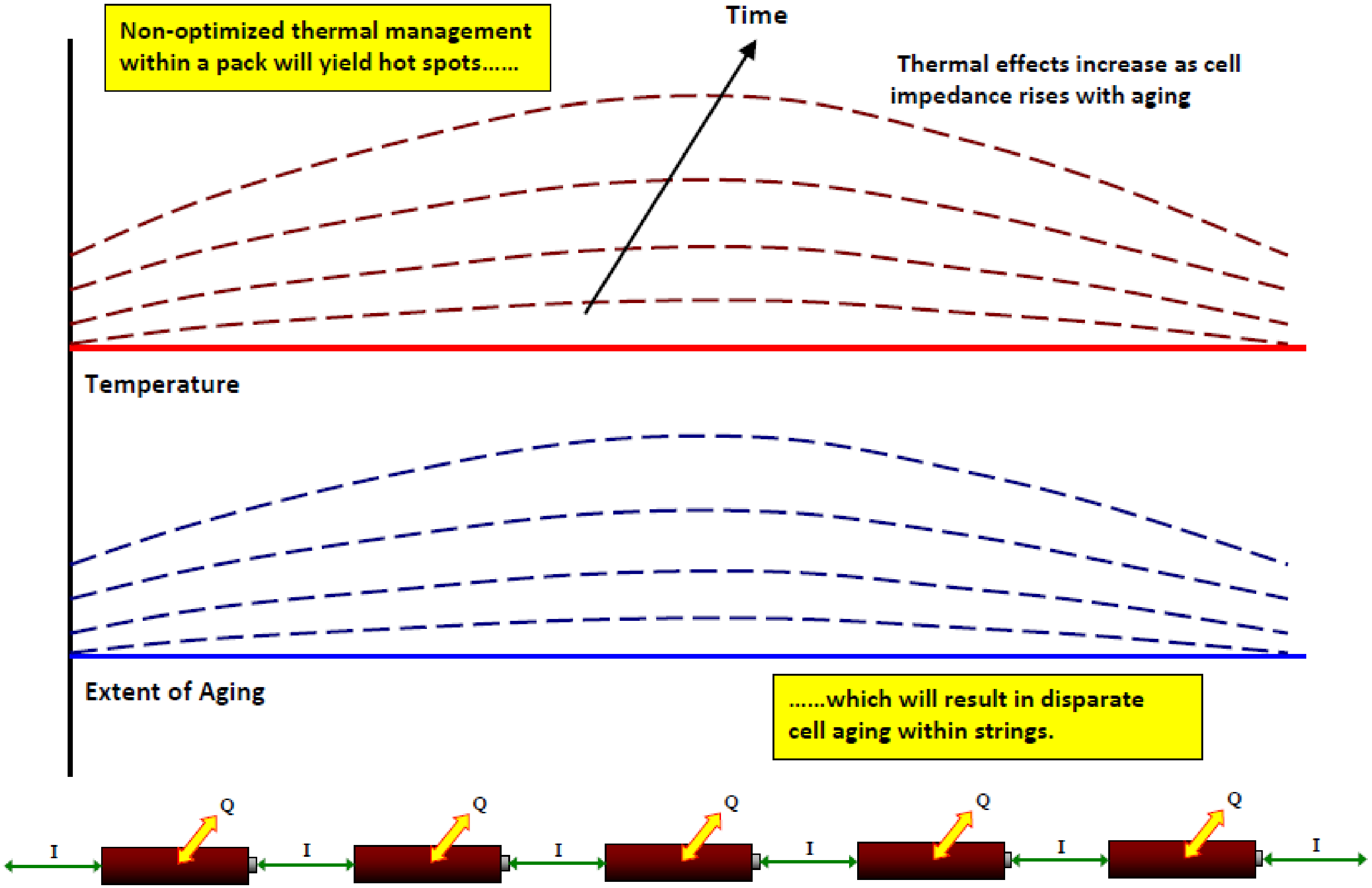
Versatile Design:

- Up to 50 psi effective cell P via pneumatic control
- Accommodates cells to 12x12-in
- Multiple cells can be stacked
- Thermal management via Peltier devices
- Modes: dynamic P management or fixed gap (static)
- Serves many pouch cell targets in diverse applications (DOE, DoD, grid storage, etc.).
- Data directly supports design of battery pressure management systems.
- Benefits: improved cell performance, stability and life through lowered, managed impedance.

Anomalies in Strings

Thermal, SOC, Cell build, etc.

A synergistic combination of DADT (INL/Hawaii), State Determination, and Prognostic Modeling (CellSage) will allow timely determination of string aging and performance.



Examples of string aging simulations will be available at the AMR.

<u>These aging effects can be modeled using INL CellSage!</u>

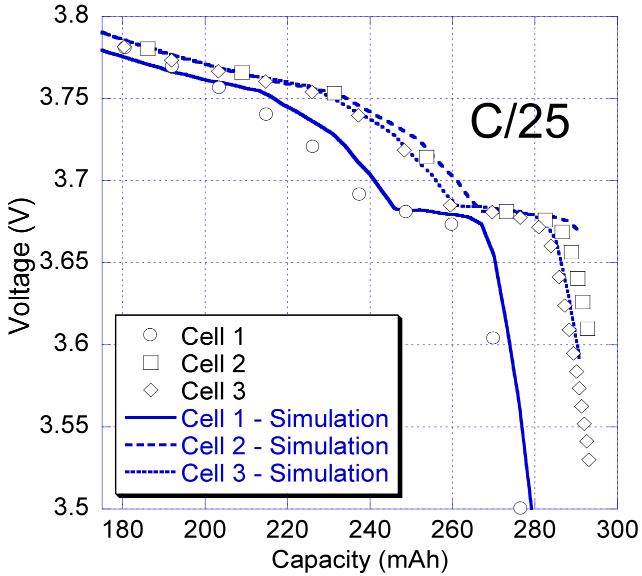
Diagnostic Studies by HNEI

- Multi-cell String Evaluation and Diagnosis (data and simulations).

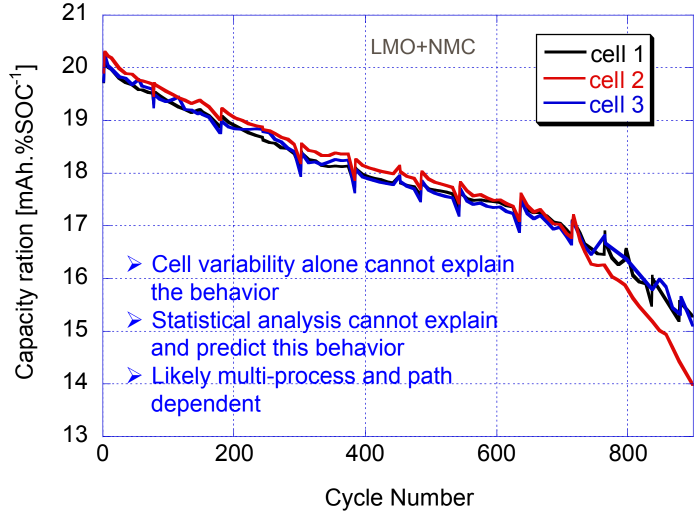
3S1P configuration testing:

- Degradation Modes Simulation (mechanistic inference technique).
- Mechanistic Diagnostics with Quantifiable Results and Symptom Presentations.

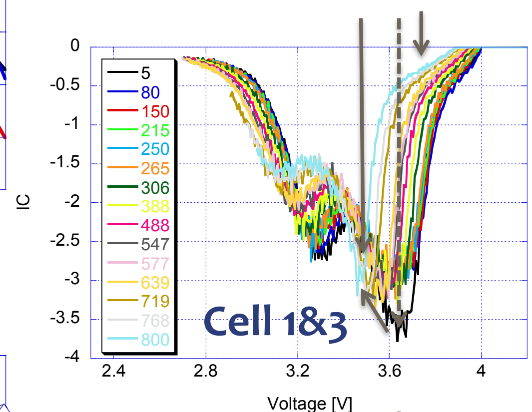
Multi-cell String Evaluation and Diagnosis

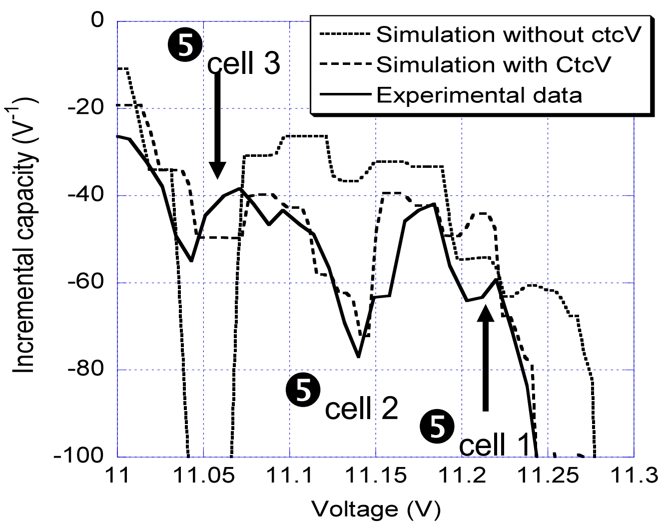


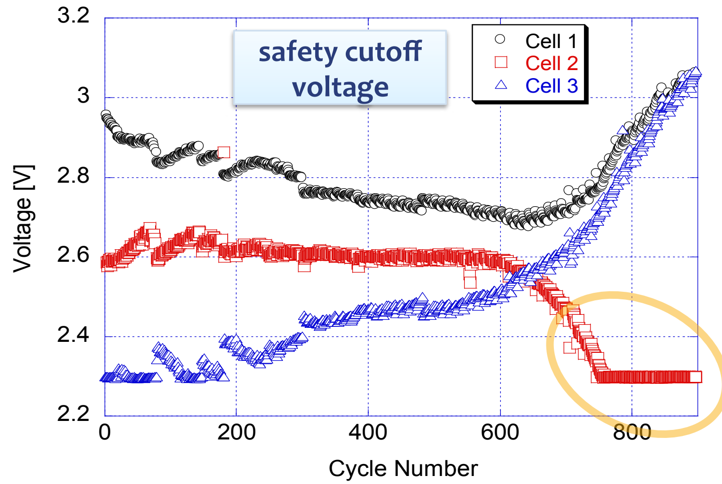
Peculiar failure mode

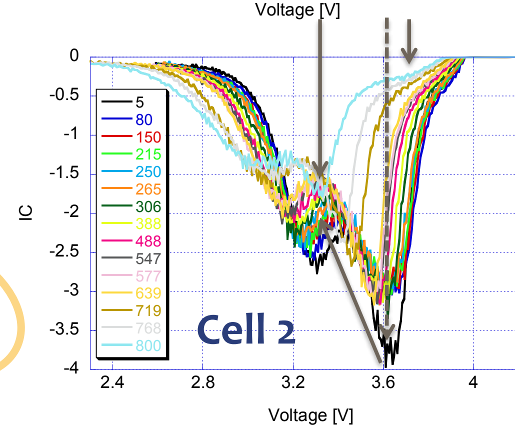


Unique failure by anisotropic over-discharge of LMO





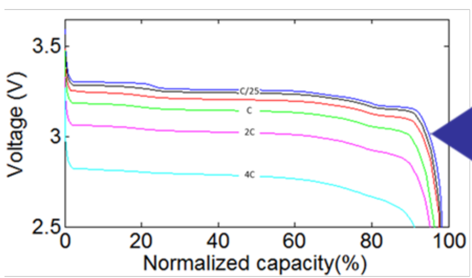


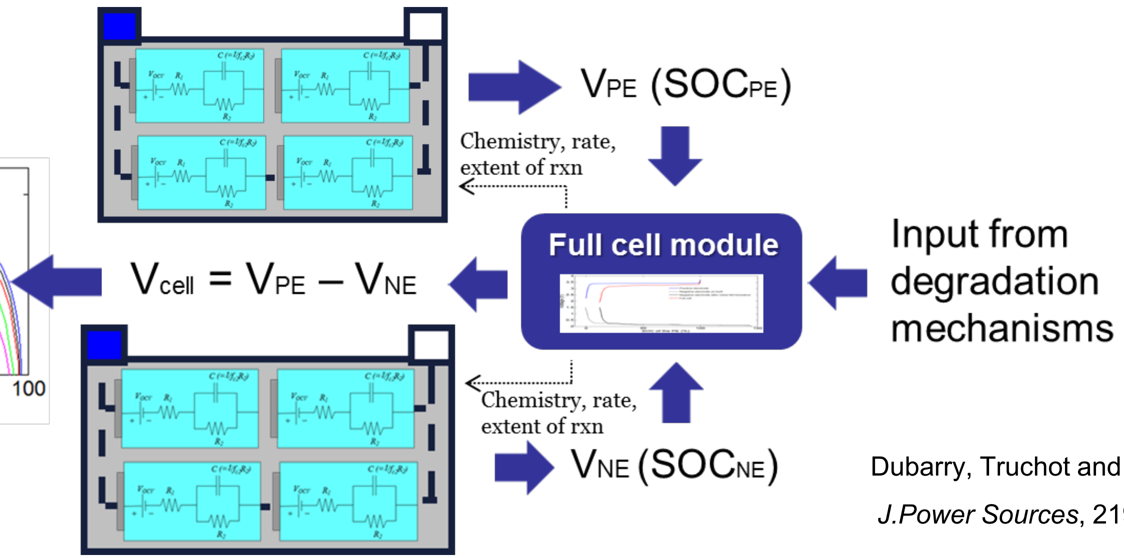


Model on cell variability

Degradation Modes Simulation

- Unique mechanistic inference technique
  - ECMs for half cells + full-cell module for electrode matching
  - Backward looking approach: choose the degradation & look for quantifiable effects on cell performance characteristics
  - Use experimental half-cell data: easy to incorporate new chemistry



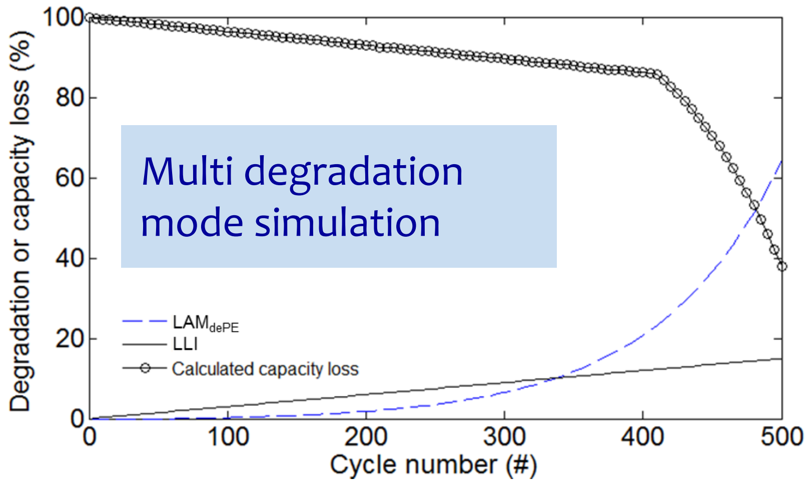


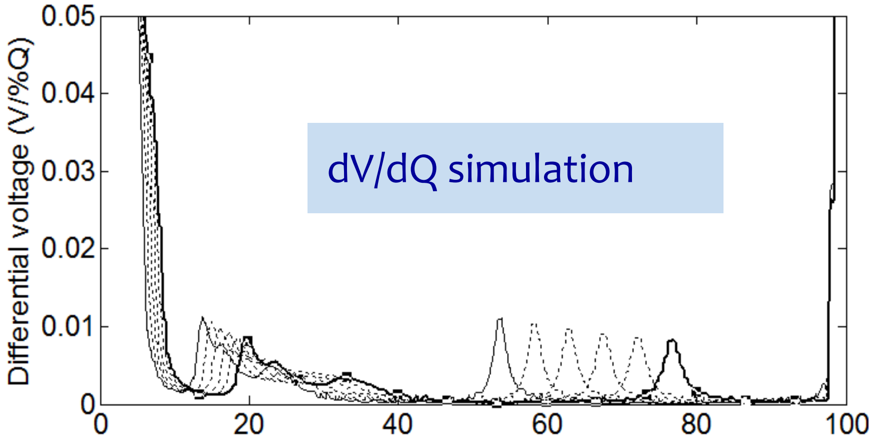
Dubarry, Truchot and Liaw, *J.Power Sources*, 219 (2012) 204-216

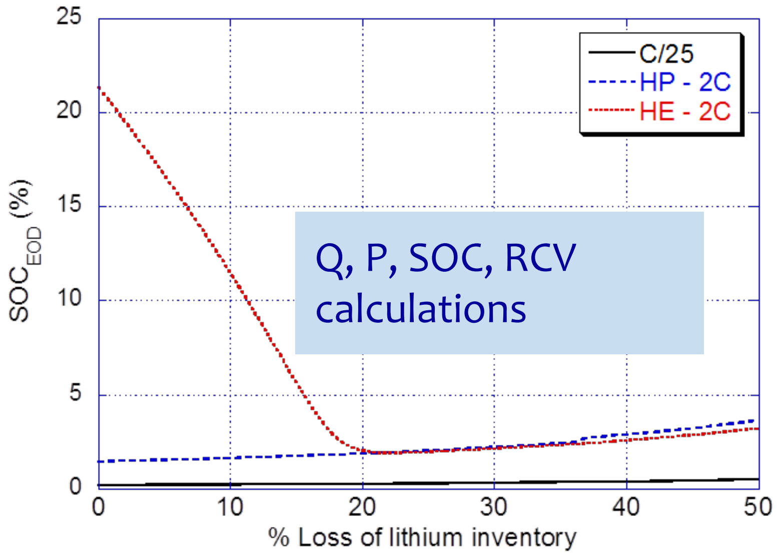
- ✓ Change in active material
- ✓ Change in lithium inventory
- ✓ Changes in ohmic and faradic resistance

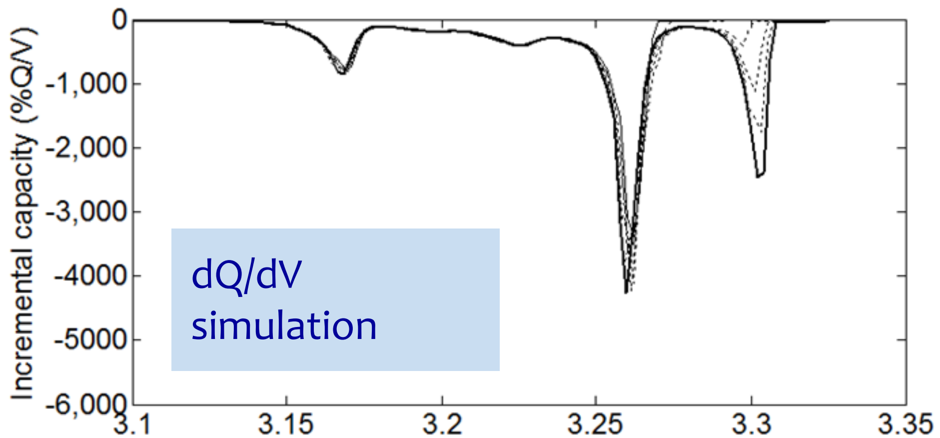
Emulates the quantifiable effects of most of the well-established degradation mechanisms

Mechanistic Diagnostics with Quantifiable Results and Symptom Presentations









Dubarry, Truchot and Liaw, *J. Power Sources*, 219 (2012) 204-216

Collaborations

- **Hawaii Natural Energy Institute.** Involved in diagnostic analysis of cell performance data to determine path dependence effects related to aging conditions tied to PHEV test protocol. HNEI work is coordinated by Prof. Bor Yann Liaw.
- **USDRIVE Program.** Initiated dialogue in 2011 regarding DADT activities as they pertain to PHEV-type cycling coupled to thermal cycling.
- **Argonne National Lab**. Provides oversight and coordination on key issues regarding the ABR program. Battery testing and modeling tasks are complementary between INL and ANL.
- **US SOCOM**. INL is leveraging resident testing and analysis techniques to evaluate novel INL electrolyte additives in a SOCOM application.

Future Work *(pending further funding)*

- **Integrate DADT findings into cell life prognostic models** (INL CellSage and UH Emulator), and determine synergy from integration of models.
- **Pouch Cell Pressure Management & Optimization**: determine if there is a common or universal range of pressure that boosts performance and prolongs longevity of pouch cells; determine best mode of pressure management (static vs. dynamic).
- **DADT with other duty cycles** (e.g., FUDS, DST), or temperature parameters defined for a particular city or region.
- **DADT on other viable ABR and commercial cells** to elucidate path dependence of aging for alternate cell chemistries (e.g., LTO or silicon anodes, phosphate-based cathodes, high voltage LMR NMC cathodes, etc.).
- **String Testing and Diagnostics**: continue this crucial test component to understand aging dynamics within a series population, as well as series/parallel configurations. Will typically involve 3-9 cells per string.
- **Post mortem Analysis of Materials**: Positron Annihilation and Ellipsometry are among two techniques we can use to determine before/after changes in surface and internal properties due to relevant aging conditions such as Daily Thermal Cycling.
- **Publish!**

Summary

- Parallel DADT studies at INL and HNEI have involved well over 100 commercial lithium-ion cells, where we have isolated the effects of foremost operational parameters on the aging path, such as magnitude of power pulses, the effects of high SOC, temperature excursions, and magnitude of daily thermal cycling during duty cycles. These studies have captured mature aging trends for diagnostic (mechanistic) analyses.
- Knowledge gained through DADT involving commercial lithium-ion cells shows
  - Aging path is unique to operational and environmental conditions that promote various irreversibilities to degradation processes.
  - Long-term testing (>12 months) is vital to detect degradation mechanisms prone to happen at test conditions aimed at EDV applications!
  - Distinct aging stages appear under more prolonged aging, e.g., operating at high SOC can produce as many as three (3) distinct stages of degradation while approaching 50% fade.
  - Daily Thermal Cycling can more than double the rate and extent of capacity loss, emphasizing the need for advanced, adaptive thermal management. This accelerated loss is believed to be due to high material stress under combined thermal and electrochemical cycling. *DTC should be considered as an accelerated aging condition for vetting EDV batteries.*
  - Cells under calendar-life conditions are more immune to thermal cycling aging effects.
  - Dynamics of string aging are complicated by cell-to-cell variations, string configuration, cell chemistry, and conditions of use. Diagnostics of string "health" remains a crucial challenge.
- Advanced Physical and Emulation Models are poised to provide accurate diagnostics/prognostic of cell and string aging. Such tools should become integrated into the technology vetting process.
- *Knowledge of Path Dependence enables Path Optimization,* which supports Battery Use Mapping.

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- Tim Murphy, INL

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HNEI

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Technical Back-Up Slides

Reference Performance Test (RPT)

The RPT is designed to facilitate Diagnostic Analysis of cell data. There are three primary components to the RPT, all assessed at 30 °C :

(A) static and residual capacity (SRC) over a matrix of current,

(B) kinetics and pulse performance testing over current for SOCs of interest,

(C) EIS for SOCs of interest (90, 70, 35%).

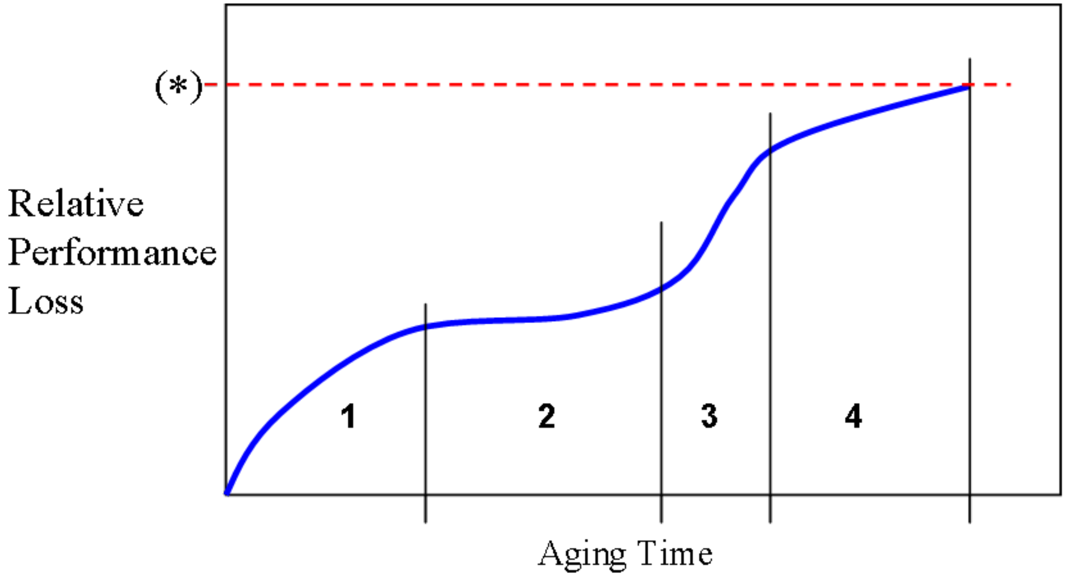
The RPT is performed on cells every 28-day test interval.

A "pulse-per-day" (PPD) is also performed to provide a quick diagnostic snapshot (20-s discharge and charge pulses at 90% SOC, 30 °C).

Approach

Path Dependence of Cell Aging

- The extent and rate of cell aging over time depends on specific operational conditions (stress factors) encountered over the timeline. Path dependence asserts that the *sequence* of aging conditions (as well as the nature of conditions) has a direct influence on the rate of aging and net aging along the timeline. Think “batch reactor”.
- A change in aging conditions can accelerate or decelerate degradation mechanisms, and can initiate new ones. Reaction kinetics and thermodynamics are key to understanding the progression of irreversible aging processes along the path.
- Cell aging should be simultaneously judged from loss of capacity, rise in impedance, loss of power, self discharge, etc., where each require a standard basis.



Shown is an idealized projection of a path dependence involving four distinct aging conditions.

Path dependence asserts that a randomized rearrangement of the four conditions will likely **not** reproduce the reference aging of (*) by the end of the fourth period, due to how irreversibilities in degradation occur between states.

ES096 feeds directly into:

(see ES124 from 2012 AMR)

Cell's Age

Cell Sage

Battery Performance Diagnostics and Prediction

Novel INL computational tools useful toward ♦cell design ♦performance characterization ♦evaluation of aging trends.

Can be integrated or embedded into numerous applications or within onboard device monitoring and control systems.

Aging trends can be predicted at arbitrary field conditions that are variable over service life, permitting direct analysis of aging path dependence, life optimization, and thermal management design.

Essential battery health metrics are covered:

- **Contributions to Capacity Loss,**
- **Contributions to Cell Conductance Loss (pulse R, EIS, IMB),**
- **Cell Kinetic performance over multiple domains,**
- **Degradation of Materials due to Daily Thermal Cycling (DTC).**

Method has been applied to multiple use scenarios, including city-wise evaluation of cell aging.

Important Model Parameters: ***singly and in combination, can be variable over time.***

- **Temperature**
- **SOC**
- **Cycling Regime (cal- vs cyc-Life)**
- **Cycling Magnitude/Freq.**
- **DTC range**
- **T-ramping under DTC**
- **City of interest**
- **Cell Chemistry**

Key Model Features

Current (I), heat (Q)

- Cells are modeled under a batch reactor scenario; **can be extended to strings**.
- General method is founded on a *Deviation from Baseline Approach,* where the baseline is an operating condition relevant to the chosen application.
- Chemical kinetic parameters for degradation mechanisms are evaluated at each unique aging condition, over several domains of battery conditions (temperature, state of charge, cycling type, etc.).
- Thermodynamic evaluations permit a reliable framework for quantifying extent of reactions and optimizing the aging path.
- Sigmoidal-based mathematics allows for self-consistent and seamless evaluations of each aging mechanism. Given a performance loss metric at aging condition i (Ψ_i) we have:

$$\Psi_i = \sum_j 2M_j \left[\frac{1}{2} - \frac{1}{1+\exp\left(a_j t^{b_j}\right)} \right]_i$$

a_j : rate constant attributable to mechanism j,

b_j : related to the order of reaction for mechanism j,

M_j : theoretical maximum limit of capacity loss under mechanism j considering the thermodynamic limit of degradation under j for a batch system.

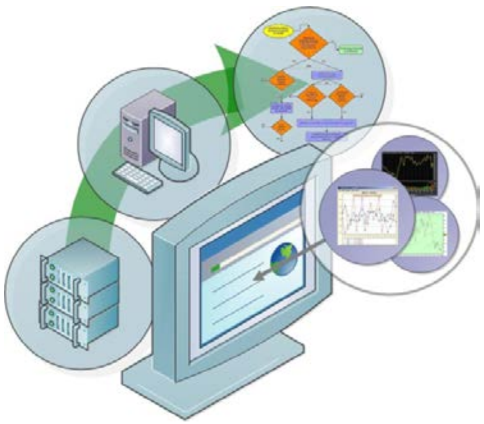
Battery Database Management System (BDMS)

(in collaboration with HNEI)

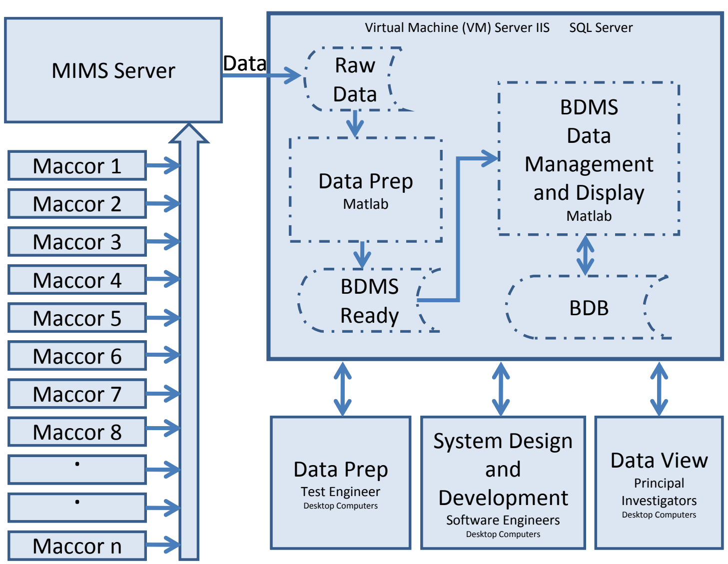
Purpose

To facilitate the efficient and timely extraction of large and numerous datasets needed for diagnostic analysis by INL and collaborators. Platform resides within a virtual environment. *This will accelerate bringing DADT knowledge to DOE and the battery R&D community.*

Significant progress has been made to build infrastructure for a dynamic database that is adaptable, expandable, trainable, and highly interactive.



Stage 1 Development



Stage 2 Development and Deployment